

(12) **UK Patent Application** (19) **GB** (11) **2 211 850** (13) **A**
 (43) Date of A publication 12.07.1989

(21) Application No 8725573.3

(22) Date of filing 31.10.1987

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(51) INT CL⁴
C08K 5/53 // C07F 9/40, C08L 25/06 71/04

(52) UK CL (Edition J)
C3K KEC K241 K242 K244 K254 K310
C2P PD P3B11A P3B11B P3B12B P3B14A P3B19B
P3B19D P3B21 P5B P7 P9
C3W W205 W215 W228 W304 W305 W310 W317
W320 W323
U1S S1362 S3011

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(58) Field of search
UK CL (Edition J) C2P, C3K

(54) Flame retardant polymer composition

(57) Halogen free polymer compositions comprise as flame retardant a metal or metalloid salt of a phosphonic acid of formula



In which R is straight or branched chain alkyl having 1 to 18 carbons, cycloalkyl having 5 or 6 carbons, alkenyl having 2 to 6 carbons, aryl having 6 to 10 carbons, aralkyl having 7 to 11 carbons, aralkenyl having 8 to 12 carbons, or monocyclic or fused bicyclic O, N or S heterocyclic, R being optionally substituted by one or more halogen, hydroxyl, amino, alkoxy, carboxy or carbalkoxy; and R' is hydrogen, straight or branched chain alkyl having 1 to 8 carbons, aryl having 6 to 10 carbons or aralkyl having 7 to 11 carbons, R' being optionally substituted by one or more halogen, hydroxyl, amino, alkoxy, carboxy or carbalkoxy; and wherein the metal or metalloid is selected from Groups IIA, IIB, IIIA, IVA, IVB, VA and VIII of the Periodic Table (Fisher Scientific Company 1968) provided that when the metal is an alkaline earth metal and R is alkyl or aryl, R is substituted by one of the above substituents and further provided that when R is alkyl with 1 to 3 carbon atoms it is substituted by amino, alkoxy, carboxy or carbalkoxy.

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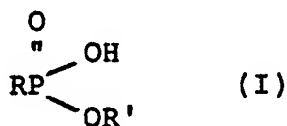
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Flame Retardant Polymer Composition

The present invention relates to flame retardant polymer compositions.

Polymers, particularly halogen-free polymers, are commonly made more flame retardant by incorporating therein a phosphorus-containing compound, a halogen-containing compound or a mixture thereof. Some polymers are processed at high temperatures of, for example, 250°C or higher, and many known flame retardants are not suitable under these conditions because they are too volatile, or not sufficiently thermally stable.

We have now found a class of compounds which are thermally stable at high temperatures and which can be used as flame retardants in a wide range of plastics. The compounds also do not give unwanted plasticising properties to rigid polymers. Accordingly the present invention provides a composition comprising a halogen-free polymer and a flame retardant amount of a metal or metalloid salt of a phosphonic acid of the general formula I



in which R is a straight or branched chain alkyl group having 1 to 18 carbon atoms, a cycloalkyl group having 5 or 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, an aryl group having 6 to 10 carbon atoms, an aralkyl group having 7 to 11 carbon atoms, an aralkenyl group having 8 to 12 carbon atoms, or a monocyclic or fused bicyclic heterocyclic group having one or more of O, N and S as hetero atoms, R being unsubstituted or substituted by one or more halogen, hydroxyl, amino, alkoxy,

and R¹ is hydrogen, a straight or branched chain alkyl group having 1 to 8 carbon atoms, an aryl group having 6 to 10 carbon atoms or an aralkyl group having 7 to 11 carbon atoms, R¹ being unsubstituted or substituted by one or more halogen, hydroxyl, amino, alkoxy, carboxy or carbalkoxy groups; and wherein the metal or metalloid is selected from Groups IIA, IIB, IIIA, IVA, IVB, VA and VIII of the Periodic Chart of Elements (Fisher Scientific Company 1968) provided that when the metal is an alkaline earth metal and R is an alkyl or aryl group, R is substituted by one of the groups, listed above, and further provided that when R is an alkyl group with 1 to 3 carbon atoms it is substituted by an amino, alkoxy, carboxy or carbalkoxy group.

When R is an alkyl group it preferably has 4 to 12 carbon atoms and may be, for example, butyl, pentyl, octyl, decyl or dodecyl.

When R is a cycloalkyl group it may be a cyclopentyl or cyclohexyl group.

When R is an alkenyl group it may be a vinyl, propenyl, butenyl, pentenyl or hexenyl group.

When R is an aryl group, it may be a phenyl or naphthyl group.

When R is an aralkyl group it may be a benzyl, phenyl ethyl or naphthylmethyl group.

When R is a heterocyclic or heteroalkyl group it may be, for example, a furan, thiophene, pyrrole, pyrazole, pyrazolone, imidazole, imidazolone, triazole, oxazole, isoxazole, pyridine, pyridone, pyrimidine, pyrimidinone, pyridazine, pyridazinone, triazine, benzimidazole, benzimidazolone, benzothiazole or benzoxazole group.

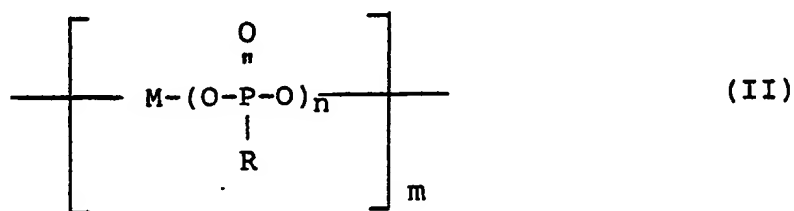
When R¹ is an alkyl group it may be a methyl, ethyl, butyl, pentyl, hexyl or octyl group.

The metal or metalloid may be, for example, magnesium, calcium, barium, zinc, boron, aluminium, tin, antimony, iron, cobalt, nickel or titanium.

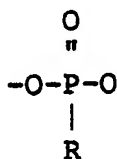
Preferably the metal is magnesium or aluminium, most preferably aluminium.

The salt may be a simple ionic compound formed between anions of the phosphonic acid and cations of the metal or metalloid.

Where R' is H and the metal or metalloid has a valency greater than one, the salt may have a polymeric structure as represented by the general formula (II)

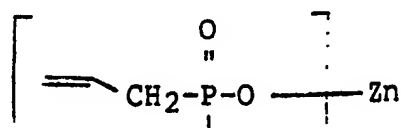
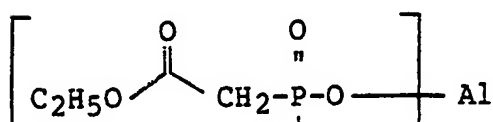


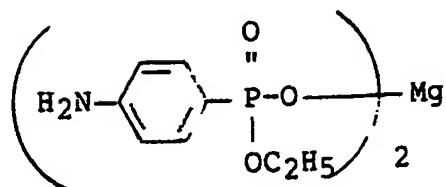
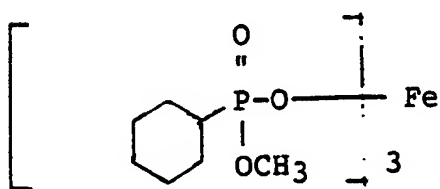
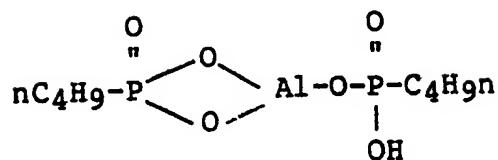
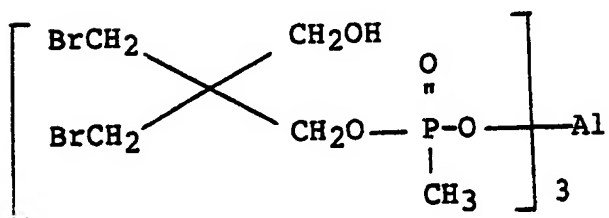
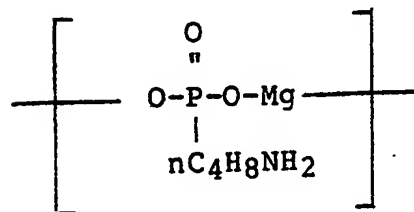
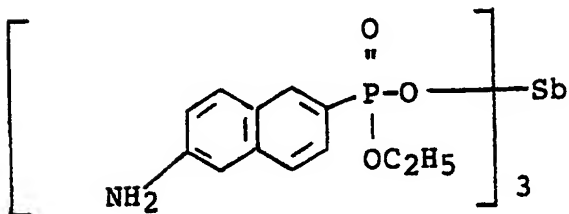
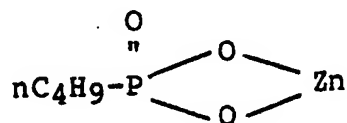
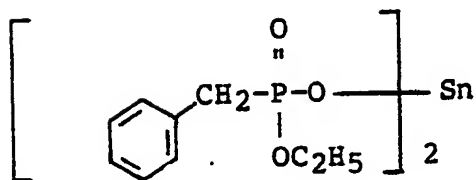
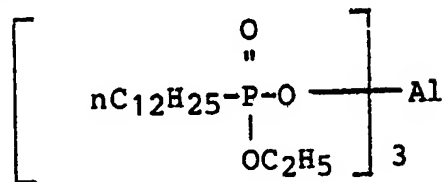
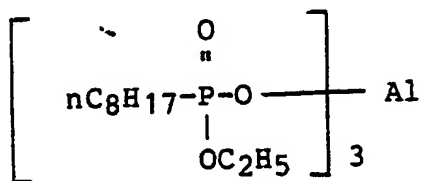
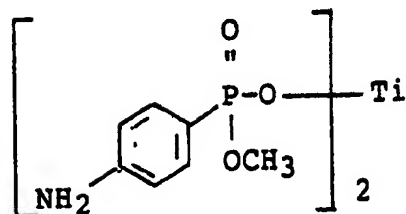
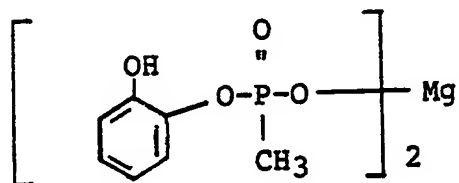
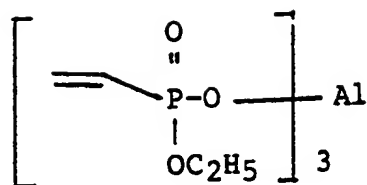
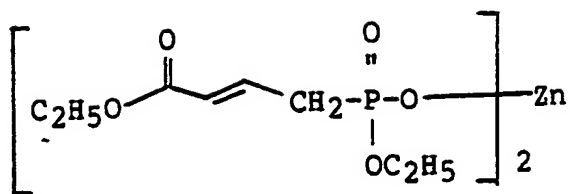
where R is as defined above, M is the metal or metalloid, n has a value one less than the valency of M and m is from 2 to 100 and where each group

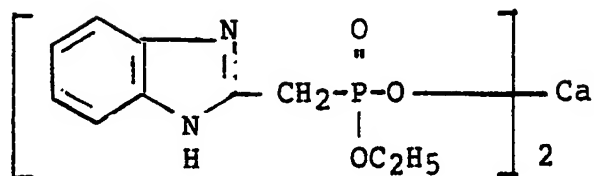
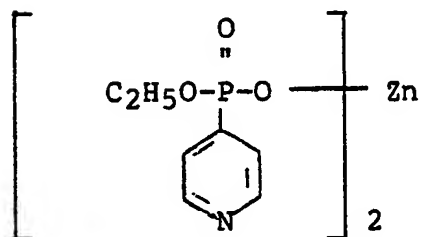
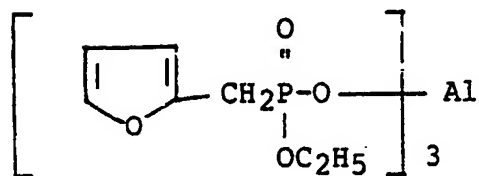
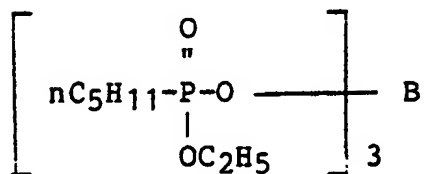
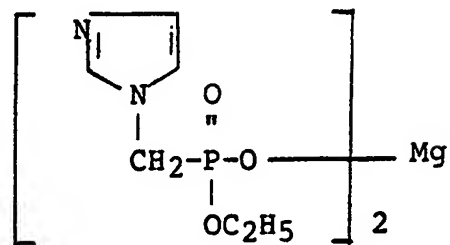
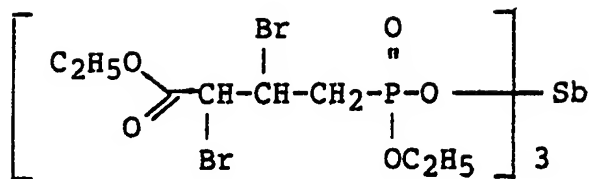
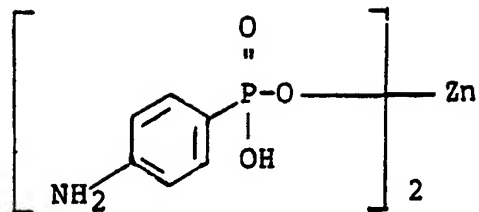
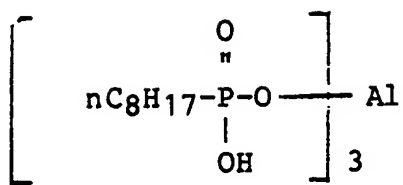


is attached to M atoms only.

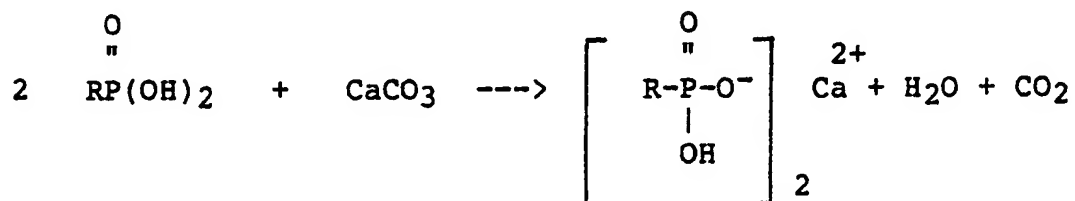
Non limiting Examples of phosphonic acid salts of the present invention are given below.



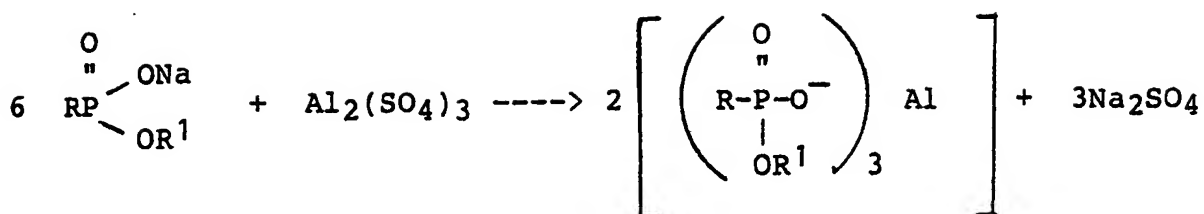




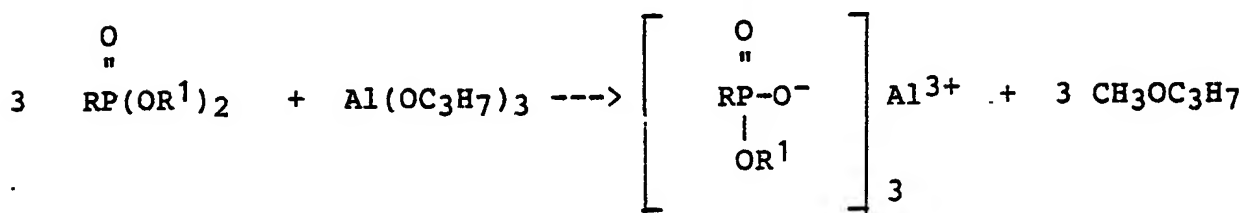
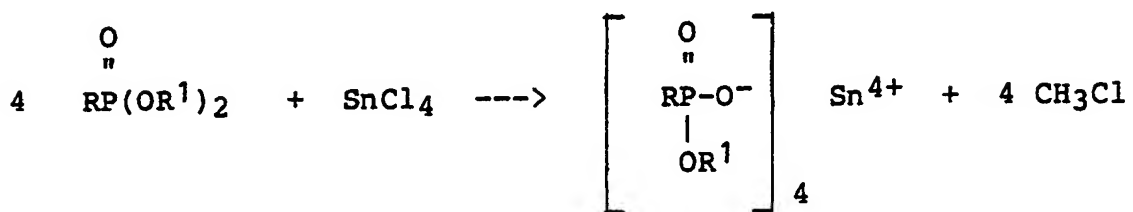
The phosphonic acid salts are either known, or can be readily prepared by known methods. The phosphonic acid or its sodium salt may be reacted with the metal carbonate or oxide, e.g.



The sodium salt of the phosphonic acid or partial ester may also be reacted in aqueous solution with a water-soluble metal



Other processes include reacting an ester of the phosphonic acid with a metal halide or metal alkoxide, e.g.



The amount of phosphonic acid salt added to the polymer as a flame retardant may be varied over a wide range. Usually from 0.1 to 100 parts are used per 100 parts by weight of polymer. Preferably there are used 0.5 to 30 parts and, most preferably, from 2 to 20 parts by weight per 100 parts by weight of polymer. The optimum amount used depends on the nature of the polymer and the actual salt used and may be readily determined by simple experiment. However, because the salts are generally effective at low levels of addition they produce less unwanted effects in the polymer than other known flame retardant additives.

The salts may be used in various physical forms depending on the polymer used and the desired properties. For instance the

salts may be ground to a finely divided form to enable better dispersion throughout the polymer. Also, mixtures of different salts may be used if desired.

The phosphonic acid salts may be used in various polymers. Examples of polymers which may be rendered flame retardant are:

1. Polyphenylene oxides and sulfides, and blends of these polymers with polyamides, polyesters such as polybutylene terephthalate, polystyrene graft and copolymers such as high impact polystyrene, EPDM copolymers with rubbers.
2. Polyurethanes which are derived from polyethers, polyesters or polybutadiene with terminal hydroxyl groups on the one side and aliphatic or aromatic polyisocyanates on the other side including polyisocyanurates, as well as precursors thereof.
3. Polyamides and copolyamides which are derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, such as polyamide 4, polyamide 6, polyamide 6/6, polyamide 6/10, polyamide 11, polyamide 12, poly-2,4,4-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide, as well as copolymers thereof with polyethers, such as for instance, with polyethylene glycol, polypropylene glycol or polytetramethylene glycols.
4. Polyesters which are derived from dicarboxylic acids and dialcohols and/or from hydroxycarboxylic acids or the corresponding lactones, such as polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylol-cyclohexane terephthalate and polyhydroxybenzoates as well as block-copolyether-esters derived from polyethers having hydroxyl end groups.
5. Unsaturated polyester resins which are derived from

with polyhydric alcohols and vinyl compounds as cross-linking agents, and also halogen-containing modifications thereof of low inflammability.

6. Polystyrene.

7. Graft copolymers of styrene, such as, for example, styrene on polybutadiene, styrene and acrylonitrile on polybutadiene, styrene and alkyl acrylates or methacrylates on polybutadiene, styrene and acrylonitrile on ethylene/propylene/diene terpolymers, styrene and acrylonitrile on polyacrylates or polymethacrylates, styrene and acrylonitrile on acrylate/butadiene copolymers, as well as mixtures thereof with random copolymers of styrene or α -methylstyrene with dienes or acrylic derivatives, for instance the copolymer mixtures known as ABS-, MBS-, ASA- or AES-copolymers.

8. Cross-linked epoxide resins which are derived from polyepoxides, for example, from bis-glycidyl ethers or from cycloaliphatic diepoxides.

9. Polycarbonates and blends thereof with other polymers such as ABS.

The compositions of the invention may also contain other conventional ingredients, such as heat stabilisers, light stabilisers, ultra-violet light absorbers, anti-oxidants, anti-static agents, preservatives, adhesion promoters, fillers, pigments, lubricants, blowing agents, fungicides, plasticisers, processing aids, other fire-retardant additives and smoke suppressants.

Other fire retardant additives which may be used with the phosphonic acid salts include phosphorus containing esters and salts such as triaryl phosphates, alkyl aryl phosphates and phosphonic acid salts, halogen, especially bromine and chlorine-

containing compounds such as haloalkyl phosphate and phosphonate esters, antimony oxide, hydrated alumina, bismuth oxide, molybdenum oxide, or mixtures of these compounds with zinc and/or magnesium oxide, hydroxide or salts.

The invention is illustrated by the following Examples.

Example 1

13.4g (0.1 mole) anhydrous aluminium chloride are added in portions to 49.2g (0.3 mol) diethylvinylphosphonate maintaining the reaction temperature below 40°C using ice-water bath cooling. On completion of addition, reaction mixture is warmed to 50°C for 2 hours, cooled to 25°C and diluted with acetone (100 millilitres). The solid product is collected, washed with acetone and dried to constant weight. There are obtained 35.6g of product having melting point >250°C and has elemental analysis: C; 31.65%, H; 5.36%, Al; 6.51%, P; 21.48%. Calculated for $C_{12}H_{24}AlO_9P_3$: C; 33.33%, H; 5.56%, Al; 6.25%, P; 21.53%.

Example 2

Using the procedure described in Example 1, reaction of 13.4g (0.1 mole) anhydrous aluminium chloride with 67.2g (0.3 mole) triethylphosphono acetate gives 50.0g of product having melting point >250°C and has elemental analysis: C; 34.86%, H; 5.91%, Al; 4.25%, P; 14.65%. Calculated for $C_{18}H_{36}AlO_{15}P_3$: C; 35.29%, H; 5.88%, Al; 4.41%, P; 15.20%.

Example 3

Using the procedure described in Example 1, reaction of 82.5g (0.33 mole) triethylphosphonocrotonate with 13.4g (0.1 mole) anhydrous aluminium chloride gives 48.0g of product having melting point >250°C and has elemental analysis C; 41.15%, H; 6.16%, Al; 3.76%, P; 13.26%. Calculated for $C_{24}H_{42}AlO_{15}P_3$: C; 41.74%, H; 6.09%, Al; 3.91%, P; 13.48%.

Example 4

Using the procedure described in Example 1, reaction of 55.8g (0.3 mole) dimethylphenylphosphonate with 13.4g (0.1 mole) anhydrous aluminium chloride gives 44.5g of product having melting point >250°C and has elemental analysis: C; 45.24%, H;

4.48%, Al; 5.16%, P; 16.82%. Calculated for $C_{21}H_{24}AlO_9P_3 \cdot H_2O$
C; 45.16%, H; 4.66%, Al; 4.83%, P; 16.66%.

Example 5

A solution of 12.6g (0.15 mole) magnesium carbonate in 100 millilitres of water is added dropwise to a solution of 56.4g (0.3 mole) O(2-hydroxyphenyl)methylphosphonic acid in 100 millilitres of H_2O at $25^\circ C$. After completion of addition, the reaction mixture is slowly warmed to reflux temperature and heated for a further period of 6 hours. The reaction mixture is cooled, filtered and the solid product is washed with acetone and dried to constant weight. There are obtained 53.3g of product having melting point $180-185^\circ C$ and has elemental analysis: C; 40.57%, H; 4.55%, P; 14.77%. Calculated for $C_{14}H_{18}MgO_9P_2$: C; 40.35%, H; 4.32%, P; 14.89%.

Example 6

Using the procedure described in Example 1, reaction of 13.4g (0.1 mole) anhydrous aluminium chloride with 62.4g (0.3 mole) diethylpentylphosphonate gives 35.2g of product having melting point $>250^\circ C$.

Example 7

Using the procedure described in Example 1, reaction of 11.1g (0.083 mole) anhydrous aluminium chloride with 62.5g (0.25 mole) diethyloctylphosphonate gives 38.3g of product having melting point $>200^\circ C$.

Example 8

Using the procedure described in Example 1, reaction of 33.4g (0.25 mole) anhydrous aluminium chloride with 171.0g (0.75 mole) diethylbenzylphosphonate gives 106.2g of product having melting point $>250^\circ C$ and has elemental analysis: C; 48.39%, H;

C; 49.09%, H; 6.06%, Al; 4.09%, P; 14.09%.

Examples 9 to 16

Compositions are made up by melt compounding at a temperature of 230°C 100 parts by weight of the plastics based on polystyrene and polyphenylene oxide, sold under the Trade Name Noryl 731, and 12 parts by weight of the salt indicated in Table 1.

The Oxygen Index (OI) is measured according to BS.2782:part 1:method 141A:1983 and the flammability tested according to the "Test for Flammability of Plastics Materials - UL 94", February 1, 1984. The results are shown in Table 1.

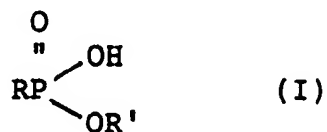
Table 1

Example	Salt from Example	OI %	UL 94
—	None	22.3	HB
9	1	24.2	VE 1
10	2	23.1	VE 1
11	3	27.6	VE 1
12	4	26.1	VE 1
13	5	22.8	VE 1
14	6	24.7	VE 1
15	7	24.8	VE 1
16	8	27.4	VE 1

These results show the flame retardant effect of the salts by virtue of an increase in OI and a higher rating in the UL 94 test, where VEO is the highest rating followed by VE1, then VE2 and finally HB (complete burning of sample)..

Claims

1. A composition comprising a halogen-free polymer and a flame retardant amount of a metal or metalloid salt of a phosphonic acid of the general formula I:



in which R is a straight or branched chain alkyl group having 1 to 18 carbon atoms, a cycloalkyl group having 5 or 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, an aryl group having 6 to 10 carbon atoms, an aralkyl group having 7 to 11 carbon atoms, an aralkenyl group having 8 to 12 carbon atoms, or a monocyclic or fused bicyclic heterocyclic group having one or more of O, N and S as hetero atoms, R being unsubstituted or substituted by one or more halogen, hydroxyl, amino, alkoxy, carboxy or carbalkoxy groups or combinations of these groups; and R¹ is hydrogen, a straight or branched chain alkyl group having 1 to 8 carbon atoms, an aryl group having 6 to 10 carbon atoms or an aralkyl group having 7 to 11 carbon atoms, R¹ being unsubstituted or substituted by one or more halogen, hydroxyl, amino, alkoxy, carboxy or carbalkoxy groups; and wherein the metal or metalloid is selected from Groups IIA, IIB, IIIA, IVA, IVB, VA and VIII of the Periodic Chart of Elements (Fisher Scientific Company 1968) provided that when the metal is an alkaline earth metal and R is an alkyl or aryl group, R is substituted by one of the groups, listed above, and further provided that when R is an alkyl group with 1 to 3 carbon atoms it is substituted by an amino, alkoxy, carboxy or carbalkoxy group.

2. A composition as claimed in Claim 1 in which R represents C₄-C₁₂ alkyl.
3. A composition as claimed in claim 1 in which the metal or metalloid is magnesium, calcium, barium, zinc, boron, aluminium, tin, antimony, iron, cobalt, nickel or titanium.
4. A composition as claimed in claim 1 in which the metal is aluminium.
5. A composition as claimed in claim 1 in which the amount of salt is from 0.1 to 100 parts per 100 parts by weight of polymer.
6. A composition as claimed in claim 5 in which the amount of salt is from 0.5 to 30 parts per 100 parts by weight of polymer.
7. A composition as claimed in claim 6 in which the amount of salt is from 2 to 20 parts per 100 parts by weight of polymer.
8. A composition as claims in claim 1 in which the polymer is a polyphenylene oxide or sulphide, or a blend of such a polymer with another polymer, a polyurethane or polyisocyanurate, a polyamide, a polyester or unsaturated polyester resin, polystyrene, a graft copolymer or terpolymer of styrene with one or more other monomers, or a cross-linked epoxide resin.